



Consommation
et Corporations Canada

Consumer and
Corporate Affairs Canada

Bureau des brevets

Patent Office

Ottawa, Canada
K1A 0C9

(11) (C) 1,293,356
(21) 506,345 ..
(22) 1986/04/10
(45) 1991/12/24
(52) 23-261

(51) INTL.CL.⁵ C22B-34/12; C01G-23/053; C01B-17/90

(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Production of Titanium Dioxide

(72) Gerken, Rudolf , Germany (Federal Republic of)
Lailach, Günter , Germany (Federal Republic of)
von Deuten, Klaus , Germany (Federal Republic of)

(73) Bayer Aktiengesellschaft , Germany (Federal Republic of)

(30) (DE) Germany (Federal Republic of) P 35 13 120.9
1985/04/12

(57) 10 Claims

Canada

OCA 3254 (10-89) 41

BEST AVAILABLE COPY

A process for the production of titanium dioxide

5

10 The present invention relates to a process for the
production of titanium dioxide by discontinuous digestion
of titanium slag with sulphuric acid, production of a
titanyl sulphate solution suitable for hydrolysis from the
solid digestion cake obtained during digestion, hydrolysis
of the titanyl sulphate, separation and calcination of the
titanium-containing hydrolyzate, evaporation of the waste
15 acid separated from the hydrolyzate and re-use of the
sulphuric acid separated from the evaporated waste acid
in the digestion of titanium slag.

20 The requirement for recycling of sulphuric acid from
the TiO_2 production process by the sulphate process is
having to be met more and more. In addition to the
expected economic disadvantages in comparison with dumping
of waste acid in the ocean, the process often encounters
technical problems.

25 A process for working up waste acids is known from
DE-A 3 327 769 and is adopted on an industrial scale. De-
pending on the local condition, however, problems can
arise here if the waste acid is to be almost completely
recycled.

30 According to the working up process currently
adopted, the waste acid is concentrated, preferably by
multi-stage vacuum evaporation, until a 60 to 70%
sulphuric acid with a low content of dissolved metal
sulphates can be separated by filtration from crystal-
lized metal sulphates.

35

Le. A. 23 707

5 Weinheim 1979). However, this stage of the process is extremely expensive with respect both to the investment costs and to the energy and maintenance costs.

It is accordingly the object of the present invention to propose a method which overcomes the above-mentioned disadvantages of the prior art in an economical manner.

10 This object can surprisingly be achieved by the following combination of measures:

- evaporation of the 60 to 75% sulphuric acid separated from the metal sulphates and containing dissolved metal sulphates under vacuum in horizontal or circulation evaporators at from 120 to 190°C to 76 to 87% H_2SO_4 (based on salt-free sulphuric acid),
- 15 mixing of the ground titanium slag with 95 to 98% sulphuric acid at from 30 to 80°C and addition of the recycled acid at a temperature of from 80 to 190°C, 20 preferably from 100 to 160°C.

The present invention accordingly relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, 25 production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydro- 30 lyzate and re-use of the sulphuric acid separated from the evaporated waste acid in titanium slag digestion, a 60 to 75% pre-concentrated sulphuric acid being separated from the solid metal sulphates and hydrogen sulphates after

35

Le A 23 707

5 In a particularly desirable embodiment of the process according to the invention, the concentration of the sulphuric acid is advantageously between 87 and 91%, preferably 88 and 90% H_2SO_4 (calculated as solids-free and salt-free acid) at the start of the digestion reaction and
10 from 35 to 70% of the required sulphuric acid is recovered as recycled acid from the process.

The necessary temperatures of the fresh acid and the recycled acid can be lowered according to the invention by grinding the titanium slag more finely.

15 The production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is preferably carried out by evaporation at from 120 to 190°C and from 40 to 150 mbar.

Horizontal evaporators with tantalum heat exchangers or circulation evaporators are particularly suitable for
20 these evaporation processes not only for reasons of energy consumption.

Valuation of the process according to the invention has to consider the fact that secondary energy can be used
25 instead of primary energy for producing the recycled acid and that the investment and maintenance costs are substantially lower compared with the prior art.

The drawing serves to illustrate the process according to the invention.

30 The fresh acid (1) required for the digestion of raw material is mixed in the digestion reactor (3) or in a preceding mixer with the ground titanium slag (2) (optionally with addition of ground ilmenite). The fresh acid should have a temperature of from 30 to 80°C,
35 preferably from 50 to 80°C. The necessary quantity of

5 The metal sulphates are partly in the form of
hydrogen sulphates and contain 60 to 75% sulphuric acid
as moisture. It is therefore advantageous to decompose
this "filter salt" thermally with formation of SO_2 and to
10 produce therefrom the 95 to 98% sulphuric acid required
as fresh acid. However, reaction with Ca compounds (DE-A
3 327 770) or a different harmless elimination process is
also possible.

Sulphuric acid losses occur mainly through the filter
salt, but also through the moisture of the solid residues
resulting from raw material digestion, the sulphuric acid
15 bound in the $\text{TiO}(\text{OH})_2$ and the unavoidable waste water. As
pre-concentrated acid, therefore, only about 40 to 60% of
the sulphuric acid used during digestion can be recovered.
With 60 to 75% H_2SO_4 , however, the concentration of this
acid is too low to allow autothermal slag digestion in
20 mixture with the necessary amount of from 95 to 98% fresh
acid.

The pre-concentrated acid (15) which still contains
about 3 to 6% by weight of dissolved metal sulphates
therefore must be evaporated in an evaporation II (16) to
25 76 to 87% H_2SO_4 (as salt-free acid), before it can be
recycled (17) for the digestion of the raw material. The
evaporation II (16) is carried out according to the inven-
tion by vacuum evaporation at 120 to 190°C. Circulation
evaporators or horizontal evaporators with tantalum heat
30 exchangers can be used as evaporator systems. Horizontal
evaporators are preferred owing to the particularly high
specific evaporation capacity (with respect to the
tantalum heat exchanger surface). Preheating of the pre-

35

Le A 23 707

Example 1 (Comparison Example)

5

17.5 t of ground titanium slag were mixed with 18 t of metal sulphate-containing recycled acid and with 13.6 t of fresh 96% sulphuric acid (20°C). The digestion reaction was initiated by addition of 1.4 t of water and introduction of 0.6 t of steam. The maximum reaction temperature of 203°C was attained after 10 minutes. After initiation of the reaction, air was blown through the mixture (for 30 minutes at 350 m³_n/h, then for 7 hours at 20 m³_n/h). After a maturing time of 7 hours, the digestion cake had a temperature of 169°C. The TiO₂ yield was 95.3%.

10

15

The digestion cake was dissolved with a proportion of the sulphuric acid-containing waste water from the hydrolyzate filtration (5.4% by weight H₂SO₄). After working up the titanyl sulphate solution, the mixture was hydrolysed using a further proportion of the sulphuric acid-containing waste water as diluent water.

20

85 t of waste acid containing 23.2% H₂SO₄ and 29.8% SO₄²⁻-(total) were separated from the hydrolyzate filtration process. The waste acid was evaporated in a 2-stage vacuum evaporator until the sulphuric acid (calculated as salt-free acid) had a concentration of 66% H₂SO₄. 31 t of 5 bar steam were used up for evaporating 47.5 t of H₂O.

25

11.3 t of sulphuric acid-containing filter cake were separated from the metal sulphate-sulphuric acid suspension after cooling to 55°C. The pre-concentrated acid (25.7 t) contained 62.8% of H₂SO₄, 32.4% of H₂O and 4.8% of dissolved metal sulphates.

30

35

Le A 23 707

5 being 160°C. The steam consumption for producing 20.0 t
of recycled acid was 10 t of 15 bar steam. The 1.3 bar
steam for preheating the pre-concentrated sulphuric acid
was produced by depressurising the 15 bar steam conden-
sate. In view of the re-use of the 120°C hot steam
10 condensate for steam production, the energy consumption
for producing the recycled acid from pre-concentrated acid
was 22,700 kJ. 0.6 t of 5 bar steam were also saved when
initiating the digestion reaction. An advantage of 33% of
the energy requirement was therefore achieved in compari-
son with the prior art.

15

Example 3

17.5 t of ground titanium slag were mixed with 13.6 t
of fresh 96% sulphuric acid (75°C). The digestion reaction
was initiated by addition of 20.76 t of recycled acid
20 (77.65% of H_2SO_4 , 16.57% of H_2O , 5.78% of MeSO_4 , corre-
sponding to 82.4% of H_2SO_4 in the salt-free acid) having
a temperature of 140°C. Air ($350 \text{ m}^3_{\text{n}}/\text{h}$) was blown through
the reaction composition until the maximum temperature of
192°C was attained after 14 minutes. 5 bar steam (180°C,
25 0.3 t/h for 20 minutes and 20 kg/h for a further 7 hours)
was then blown through the reaction composition. After
stopping the steam, the temperature of the digestion cake
was 172°C and the TiO_2 yield was 95.2%.

30

The remainder of the process was carried out as in
Example 1. Evaporation II during which 25.7 t of pre-
concentrated acid were evaporated to 20.76 t of recycled
acid was carried out at 60 mbar in the same horizontal
evaporator as in Example 2. The pre-concentrated acid

35

Le A 23 707

Table 1

5

Exp. Fineness of grinding		T ₁	T ₂	T ₃	T ₄	t
No.	% by weight <40 μm	[°C]	[°C]	[°C]	[°C]	[min]
10	1	81	50	110	76	-
	2	81	50	140	91	106
	3	81	70	140	101	154
	4	81	80	140	109	193
	5	81	70	160	117	192
15	6	100	50	120	86	168
	7	100	50	140	95	185

20 The experimental results show that the temperature of the recycled acid can be lower if the titanium slag is ground more finely (Experiment 7) than with a coarser grinding (Experiment 2) achieving approximately the same reaction rate. Also the temperature of the 96% fresh acid can obviously be lowered instead of the temperature of the recycled acid.

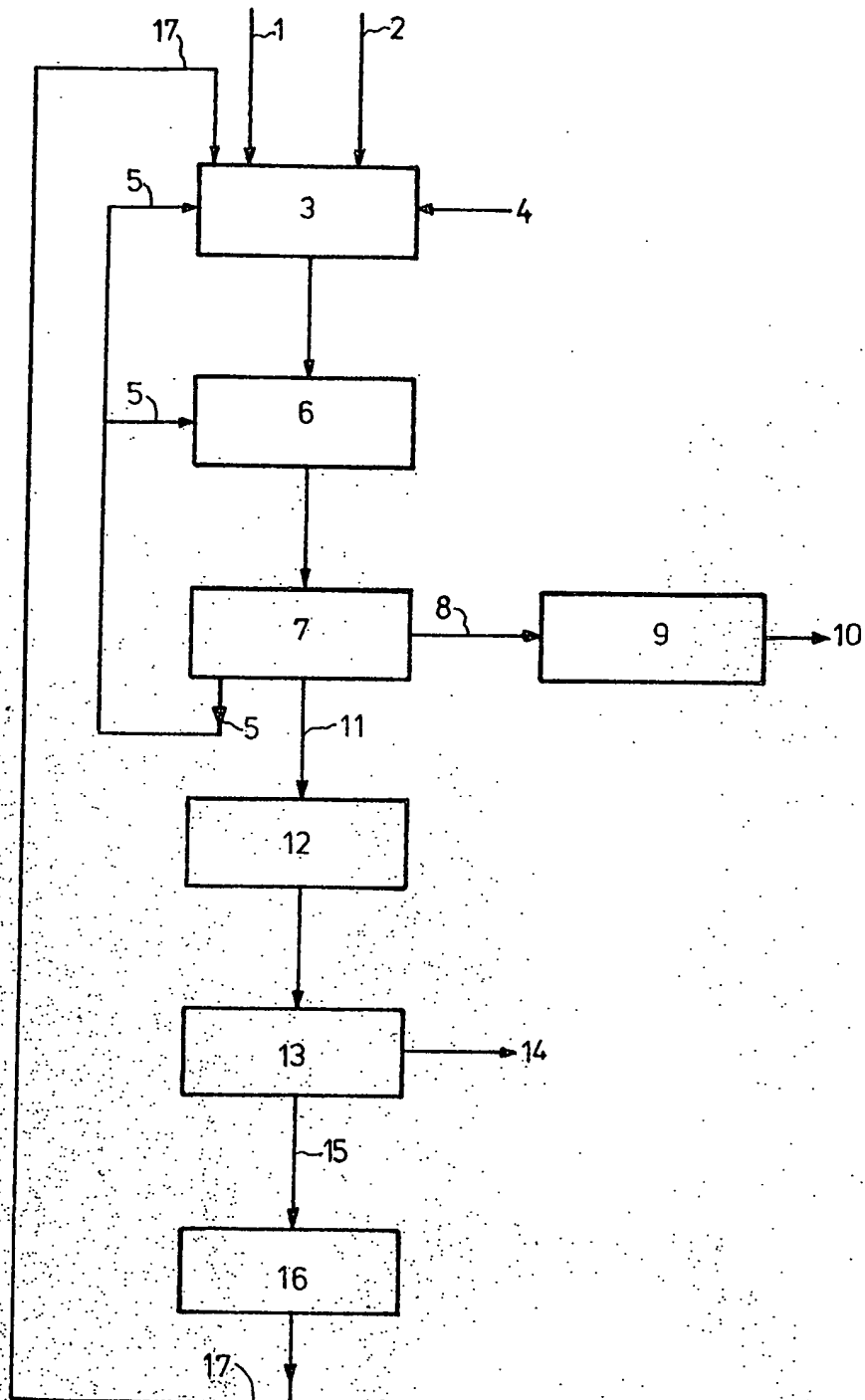
25 The slower rise in the temperature of the laboratory digestions in comparison with the rise in temperature on an industrial scale is due to the relatively high thermal losses.

30

35

Le A 23 707

5. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76-to 87%-sulphuric acid ("recycled acid") at from 100 to 160°C.
6. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 87 and 91% H_2SO_4 (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
7. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 88 and 90% H_2SO_4 (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
8. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar.
9. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a horizontal evaporator with a tantalum heat exchanger is used as evaporator.
10. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric



Le A 23 707

*Patent Agents
Green & Co. 7/2*

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☒ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.